

A Mechanistic Investigation of Nitrogen Evolution and Corrosion with OxyCombustion

Dale R. Tree (PI), Thomas H. Fletcher (co-PI), Larry L. Baxter (co-PI), Andrew J. Mackrory
Shrinivas Lokare, John Sowa, Kolbein Kolste, Brent Poole, Randy Shurtz, and James Kendall

Advanced Combustion Engineering Research Center
Brigham Young University, Provo, Utah

Background and Objective

- Pilot scale **pulverized coal** oxy-fuel tests show an unexpected reduction in NO_x emissions
- Early research (Okazaki and Ando, 1997) suggests that reduction of recycled NO_x is the dominant mechanism but...
- ...the mechanisms behind this reduction are not yet understood (Sarofim, 2007).

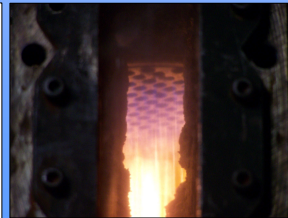
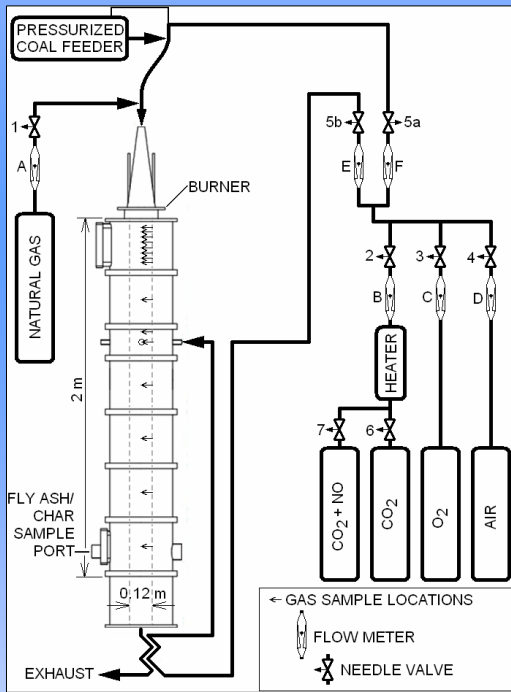
Objective:
Gain understanding of oxy-fuel NO_x reduction mechanisms through:

- Measurements of nitrogen species and other combustion products in Air and Oxy-fuel conditions
- Flat flame burner coal devolatilization experiments in N_2 and CO_2 based gases
- Detailed kinetic modeling of the experiments

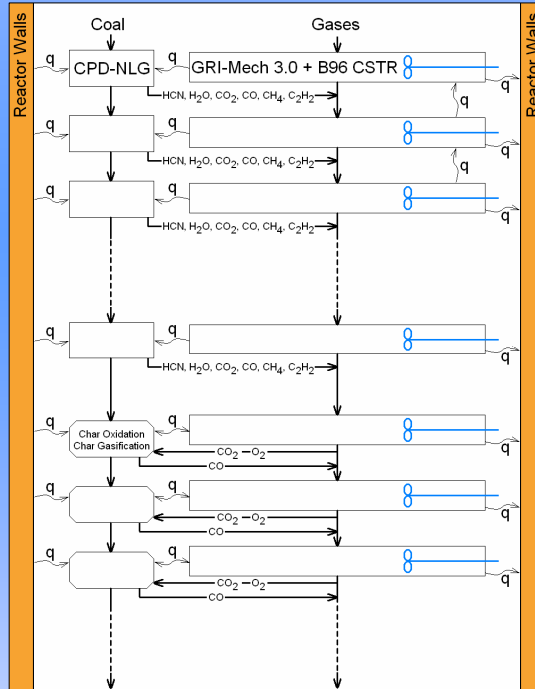
Possible NO_x Reduction Mechanisms

- Near-elimination of thermal- and prompt- NO_x
- More attached flame
- Elevated NO concentrations
- Reduction of recycled NO_x in fuel-rich zones
- Temperature increases
- Increased residence time in fuel-rich regions
- Equilibrium considerations
- Reduced NO formation from char
- Enhanced heterogeneous reburning
- Increased importance of gasification reactions

Experiment Setup



Kinetic Model Design



Oxy-fuel combustion is modeled in MATLAB using Cantera for gas phase kinetics, and the CPD-NLG model for devolatilization and fuel-N release.

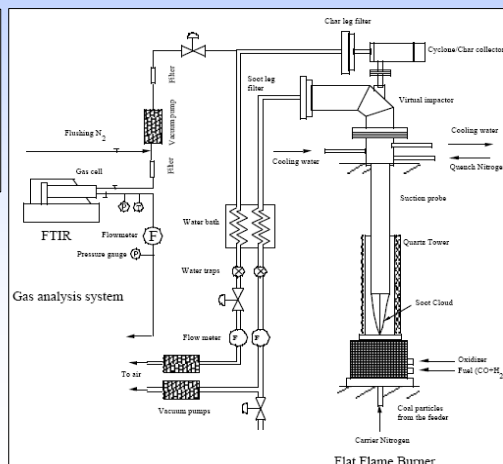
A series network of CSTR's simulates a plug flow reactor (1-D).

Homogeneous NO_x mechanisms:

- Thermal
- Prompt
- Fuel
- Advanced reburning

Char combustion & gasification uses kinetic constants from the literature specific to the coals used.

Flat Flame Burner



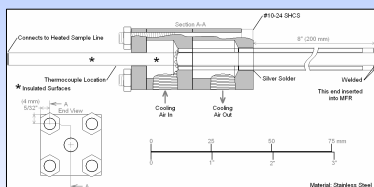
NO_x Data Analysis

NO_x concentrations can be higher in oxy-fuel than air combustion because the recycled flue gas has a lower volume flow rate than the N_2 from air that it replaces. To make a fair comparison of nitrogen evolution the effect of the dilution is removed by calculating nitrogen conversion efficiency:

$$\eta_N = \frac{N \text{ in } \text{NO}_x}{\text{Fuel} - N}$$

Assumption: All NO_x is fuel NO_x

$$\eta_N \approx \frac{\dot{m}_{\text{prod, wet}} (1 - Y_{\text{moist, prod, wet}}) X_{\text{NO}_x, \text{dry}} \frac{MW_N}{MW_{\text{prod, dry}}}}{\dot{m}_{\text{coal}} Y_{N, \text{coal}}}$$



Air-cooled Gas Sample Probe

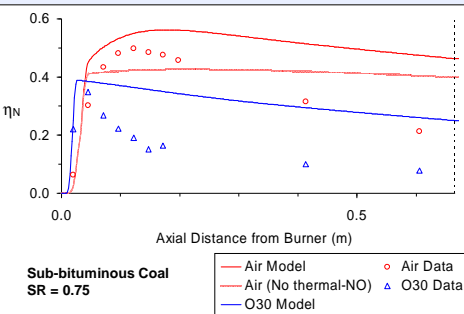
Sampled gases are rapidly quenched and pumped at 150-180°C to an FTIR gas analyzer for measurement of CO , CO_2 , H_2O , NO , N_2O , NO_2 , NH_3 , HCN , SO_2 , CH_4 , C_2H_4 . The sample is then cooled, dried, and analyzed for O_2 (zirconium oxide sensor) and NO_x (chemiluminescence)



A Mechanistic Investigation of Nitrogen Evolution and Corrosion with OxyCombustion

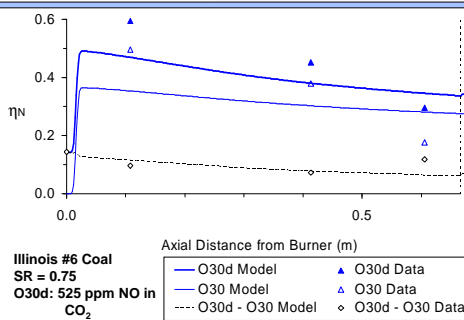
Results

Model and Data Comparisons



The kinetic model under-predicts rates of NO destruction but does correctly predict:

- Similar and rapid initial NO_x formation from volatiles
- Slower thermal NO_x production in the air case
- Shape of both air and oxy-fuel NO_x profiles

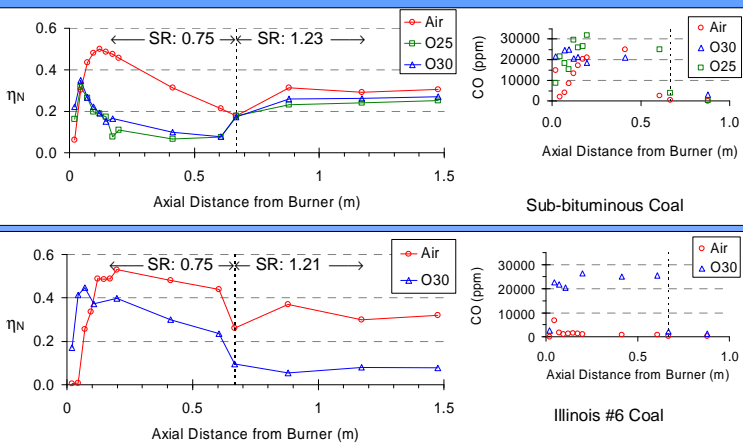


When the recycle stream contains NO the kinetic model correctly predicts trends:

- Suppression of initial NO formation (as observed by Okazaki and Ando, 1997)
- Increased rates of NO destruction



NO and CO Observations



It was noticed that the difference in effluent η_N between air and oxy-fuel correlated qualitatively with the difference between CO in the fuel-rich region.

Conclusions

From experiments at identical stoichiometry:

- Oxy-fuel combustion can produce lower NO_x emissions than air combustion independent of the reduction of recycled NO_x
- Oxy-fuel combustion can produce higher CO concentrations than air in fuel-rich regions
- When the recycle stream contains NO
 - Initial formation of NO_x from the fuel is reduced
 - NO_x destruction rates increase

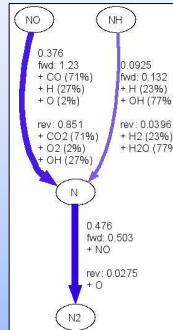
From Modeling:

- The source of high CO concentrations in oxy-fuel combustion is primarily thermal dissociation of CO₂ at high temperature (above about 1500 K)
- Gasification of the char by CO₂ in oxy-fuel combustion is a secondary cause of high CO levels in fuel rich regions of oxy-fuel combustion
- In the absence of thermal NO_x, air and oxy-fuel flames should have similar levels of initial NO formation from nitrogen in the volatiles

References

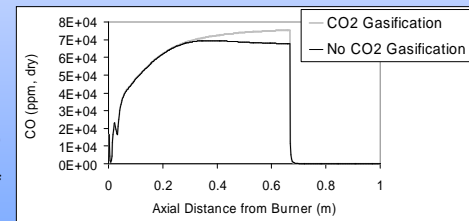
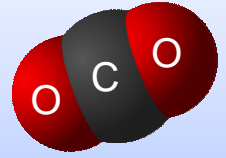
- Andersson, K, F Normann, F Johnsson (2007) Experiments and modeling on oxy-fuel combustion chemistry during lignite firing, The 32nd International Technical Conference on Coal Utilization and Fuel Systems, June 10-15, 2007, Clearwater, FL.
- Okazaki, K, T Ando (1997) NO_x reduction mechanism in coal combustion with recycled CO₂, Energy, Vol. 22, No 2/3, 207-215.
- Sarofim, A (2007) Oxy-fuel Combustion: Progress and Remaining Issues, 2nd IEAGHG International Oxy-combustion Workshop, January 25-26, 2007, Windsor, CT.

Role and Source of CO in Oxy-fuel



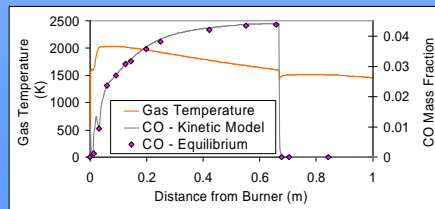
Pathway diagrams generated from the kinetic model indicate that CO and NO are important reactants on the dominant NO reduction pathway.

Both CO and NO can occur in higher concentrations in oxy-fuel reducing zones.



Lower wall temperatures in oxy-fuel cases combined with the high CO levels led to a computational investigation of the importance of CO₂ gasification.

Results indicate that gasification plays a minor role in determining the level of CO.



Comparisons of kinetic predictions with equilibrium calculations for the predicted gas mixture indicate the high levels of CO are due to thermal dissociation of the CO₂ in oxy-fuel.

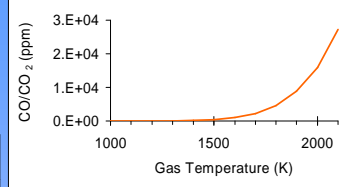
Equilibrium calculations also indicate that CO₂ dissociation will become significant at about 1500 K and will exhibit strong temperature sensitivity.

This behavior is observed in the data of Andersson et al. (2007) ↓

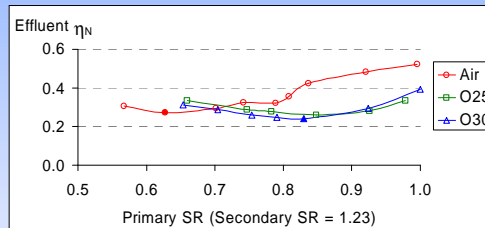
T _{gas} (K)	CO (vol%, dry)	NO (ppm, dry)	Oxidizer
1476	<0.5	~540	OF25*
1534	>7	<100	OF27*

Location: 215 mm from burner on centerline

* Indicates vol% O₂

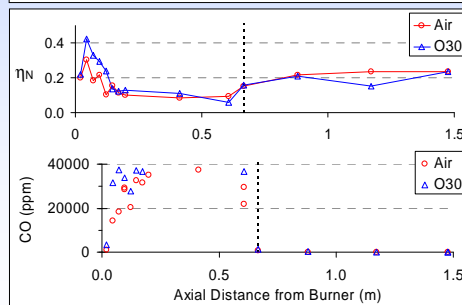


Air and Oxy-fuel Comparison: Minimum NO_x Conditions



When varying the depth of oxidizer-staging both air and oxy-fuel cases show a minimum in NO_x emissions.

- The minima occur at about the same level of effluent NO_x (in the absence of NO_x recycling).
- The stoichiometry to obtain the minimum is quite different between air and oxy-fuel: Air requires deeper staging with corresponding lower levels of burnout expected.



When both minimum η_N cases are examined in detail the η_N and CO profiles are very similar. The air case does not exhibit thermal NO_x formation.